according to Tscha's paraphrase of L&L's argument

\[ T < 0 \Rightarrow \left( \frac{\partial S}{\partial V} \right)_T < 0 \Rightarrow \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_S \Rightarrow \frac{\partial S}{\partial T} < 0 \]

for such a system, a decrease in internal energy, \
\[ \text{as by conversion of internal energy into macroscopic} \]
\[ \text{center-of-mass motion (which would violate Pbo 4, p. 12)} \]

The question of an absolute temperature scale is addressed in \( \S \ V \) (p. 61). 
For now, we assume that such a scale exists.

\[ \begin{align*}
\hat{D}S &= \left( \frac{\partial S}{\partial \mathbf{T}} \right)_{\mathbf{V}} = \int_{T_i}^{T_f} dT \left( \frac{\partial S}{\partial T} \right)_V \\
&= \frac{T_f}{T_i} \left( \frac{C_P}{C_V} \right) \left( T_f - T_i \right) > 0 \\
&= \text{positive \"measure of irreversibility\", \text{entropy increase of system}} \\
&= \text{entropy decrease of reservoir} \\
\end{align*} \]

In \( n \) steps by making contact with reservoirs at a succession of \text{temperatures} \( T_1 < T_2 < \ldots < T_n = T_f \)

\[ \hat{D}S = \sum_{j=1}^{n} \frac{T_j}{T_{j-1}} \left( \frac{C_P}{C_V} \right) \left( T_j - T_{j-1} \right) = 0 \]

in the limit of a large number of steps.

\[ \text{No increase in entropy, so no path is reversible} \]
IV. The Energy Scheme

The fundamental equation and associated stability criteria can be cast in different forms that depend on the choice of independent variables.

The fundamental equation (or any of the primitive fundamental equations),

\[ S = S(U, X_2, \ldots, X_{r+1}) \]

may be solved for the energy

\[ U = U(S, X_2, \ldots, X_{r+1}) \]  

"entropy scheme"

"energy scheme"

We can go from the entropy scheme to the energy scheme in the vicinity of a point \( S_0, U_0 \) provided

\[ \left( \frac{\partial S}{\partial U} \right)_0 \neq 0. \]

Conversely, the entropy scheme can be regained from the energy scheme in the same vicinity provided

\[ \left( \frac{\partial U}{\partial S} \right)_0 \neq 0. \]

According to the first of these conditions, a switch to the energy scheme cannot be made as \( \frac{\partial S}{\partial U} = \frac{1}{T} \) approaches zero, i.e., as \( T \to \infty \).

The corresponding uncertainty in \( S \) as a function of \( U \) as \( \frac{\partial U}{\partial S} = T \) approaches zero is resolved by the postulate (PcZ, p. 14) that assigns \( S \) the value zero at \( T = 0 \).
In the energy scheme, conservation of entropy replaces the conservation of energy that was a feature of the entropy scheme. For a composite system with two subsystems, the exchange of additive invariants in virtual processes obeys the relations
\[ \Delta S' + \Delta S'' = 0; \quad \Delta X'_i + \Delta X''_i = 0, \quad i = 2, 3, \ldots, t+1. \]

This condition means that the process is reversible.

We can introduce a work reservoir, whose operation in-and-of itself incurs no entropy change (think of weights and frictionless pulleys), to compensate for energy nonconservation in either a virtual process (for which such compensation isn't really necessary) or an actual process (where it is).

Tisza notes that one might naturally use the energy scheme - with built-in entropy conservation - to treat adiabatic volume changes \((\Delta V)_s\) such as those occurring in sound waves. On the other hand, one would prefer the entropy scheme - with built-in energy conservation - to treat free expansion \((\Delta V)_u\).
The stability of a particular state of a thermodynamic system depends on whether or not any of the virtual processes can actually occur. In the entropy scheme, this question is decided by the entropy maximum principle; in the energy scheme, it is decided by the energy minimum principle.

**Entropy scheme**: entropy maximized at constant energy

**Energy scheme**: energy minimized at constant entropy
Criterion of stability in the energy scheme

\[ 0 = \Delta V' + \Delta V'' \]
\[ 0 = \Delta S' + \Delta S'' \]

The total volume and total entropy are conserved by a rigid, adiabatic enclosure.

If \( \delta W = 0 \) in any infinitesimal change between constrained equilibrium states, then the initial one represents an "equilibrium" state. This equilibrium is stable by which we mean local equilibrium.

is, in addition \( \Delta W \geq 0 \) for all, even non-infinitesimal changes of state.

The initial state is at least metastable if \( \delta^2 W > 0 \) for all displacements. There is an essential instability if \( \delta^2 W < 0 \) for some displacements.

A minimum amount of work

\[ \Delta W = \Delta U' + \Delta U'' \]

must be done by an external device to effect a displacement from equilibrium to a constrained equilibrium state. Conversely, \( -\Delta U' - \Delta U'' = |\Delta U' + \Delta U''| \) is the maximum work available in the reverse transition.
For the theory to be consistent, the equilibrium conditions specified by maximum entropy (at fixed energy) and minimum energy (at constant entropy) must be equivalent, leading, in particular, to the same equilibrium state.

Let's first assume that a state is unstable by the energy criterion. This means that there is another state available the transition to which would be accompanied by a decrease in energy $W = \Delta U' + \Delta U'' < 0$ at constant entropy $\Delta S' + \Delta S'' = 0$. The work $|W|$ done by the system in this process could be returned to it as heat (how might this be accomplished?). Because $T = (\delta S / \delta U)^{ad}$ is positive, $\delta S = \frac{1}{T} \delta U$ leads to an increase in the entropy of the system; so the original state was unstable by the entropy criterion as well. Conversely, if the initial state is assumed to be unstable by the entropy criterion, then there is a state for which $\Delta S' + \Delta S'' > 0$ and $\Delta U' + \Delta U'' = 0$. Removing heat by contact with a thermal reservoir (or a series of them at sequentially decreasing temperatures) leads to $\Delta S = 0$, $\Delta U < 0$, so the original state was unstable also with respect to the energy criterion.

* Is the original state the same in these two examples, are the final states the same as well?
Our argument for disequilibrium under the energy criterion implying disequilibrium under the entropy scheme and vice versa depends on the postulate \((P<1)\) that the temperature is positive. Tisza also asks how this argument would go in a system with negative temperature.

He first considers a composite system represented by point \(A\) in a diagram like this:

The system comprises two subsystems, of appropriate sizes, in states \(B\) and \(C\), so \(A\) is a state of constrained equilibrium. (How do we determine the relative sizes of the two subsystems?)

If an internal constraint preventing heat transfer between the subsystems is removed, the system reequilibrates in state \(E\) with an entropy increase \(\Delta S = AE\); this process is evidently irreversible. If the system is coupled to a work reservoir and allowed to reach equilibrium reversibly, it performs the maximum available work

\[ -\Delta U = DA \]
The diagram looks different in the negative-temperature case (why?):

The irreversible attainment of equilibrium after release of an internal thermal constraint proceeds similarly to the positive-temperature case, with an entropy increase \( \Delta S = A'E' \). In this case, however, if work were performed reversibly on the system increasing its energy at constant entropy to reach state \( D' \), it could then undergo a spontaneous change to state \( E' \) while simultaneously increasing its entropy by \( \Delta S = A'E' \) and returning the work - \( \Delta U = A'D' \) to a work reservoir.

Can you conceive of a device that would be able to function as the "reversible work reservoir" in these two situations?
A digression provoked by Tisza's Fig. 1.

I became puzzled by some aspects of the processes described in connection with Fig. 1 and wanted to see if things could be clarified by considering a concrete example of the type of composite system illustrated there.

Let's investigate the simplest possible system: one mole of a monatomic ideal gas. In equilibrium, this system obeys an equation of state \( pV = RT \); its internal energy and temperature are related by \( U = \frac{3}{2}RT \).

Points B and C in Fig. 1(a) then correspond to (unconstrained) equilibrium states with \( (U, V, N) = (U_B, V, N_a) \) and \( (U, V, N) = (U_c, V, N_a) \) respectively.

\[ S_B = S(U_B, V, N_a) \quad \text{and} \quad T_B = \frac{3U_B}{3R} \]

\[ S_c = S(U_c, V, N_a) \quad \text{and} \quad T_c = \frac{3U_c}{3R} \]

Hence the constant-volume heat capacity takes the temperature-independent value \( \frac{\partial U}{\partial T} = \frac{3}{2}R \).
The point A is a constrained equilibrium state; here the mole of gas is divided into two subsystems that are thermally isolated from each other by an adiabatic partition. Subsystem 1 comprises \(1-x\) moles occupying \(V_1 = (1-x)V\) with internal energy \(U_1 = (1-x)U_B\) (and \(T_1 = \frac{2U_1}{3(1-x)R} = \frac{2U_B}{3R} = T_B\)). Subsystem 2 has \(x\) moles of B gas in volume \(V_2 = xV\) and internal energy \(U_2 = xU_c\) (hence temperature \(T_2 = T_c > T_1\)). The fraction \(x\) is determined by a "lever rule": We require that \(U_1 + U_2 = U_A\). Thus

\[
U_A = (1-x)U_B + xU_c = (1-x)U_B - (1-x-1)U_c
\]

which implies

\[
U_c - U_A = (1-x)(U_c - U_B)
\]

It also follows that

\[
U_A - U_B = x(U_c - U_B)
\]

so we have

\[
\frac{U_c - U_A}{U_A - U_B} = \frac{1-x}{x}
\]
If the adiabatic partition is rendered _diathermic_, then heat will flow from subsystem 2 to subsystem 1.

\[ \Delta U_1 = (1-x)U_E - (1-x)U_B \]
\[ = (1-x)(U_E - U_B) \]
\[ = (1-x)(U_A - U_B) \]

\[ U_E = U_A , \text{ since there's no change in the total internal energy.} \]

and

\[ \Delta U_2 = xU_E - xU_C \]
\[ = x(U_E - U_C) \]
\[ = x(U_A - U_C) . \]

Our lever rule ensures that

\[ \Delta U_2 = -(1-x)(U_A - U_B) = -\Delta U_1 , \]

as it must.

This transition from the constrained state A to the unconstrained state E, at constant total energy \( U_A \), is accompanied by an increase in entropy

\[ \Delta S = \Delta S_1 + \Delta S_2 \]
\[ = S_E - S_A . \]
\[
dS_1 = \frac{1}{T_1} dU_1 = \frac{3}{2} (1-x) R \frac{dT_1}{T_1}
\]
can be integrated to yield

\[
\Delta S_1 = \frac{3}{2} (1-x) \ln \frac{T_E}{T_B} = \frac{3}{2} (1-x) \ln \frac{U_A}{U_B}
\]

Similarly,

\[
\Delta S_2 = \frac{3}{2} x R \ln \frac{U_A}{U_C}
\]

Hence the total entropy change is

\[
\Delta S = \frac{3}{2} R \ln \left[ \left( \frac{U_A}{U_B} \right)^{1-x} \left( \frac{U_C}{U_A} \right)^{x} \right]
\]

\[
= \frac{3}{2} R \ln \left[ \frac{U_A}{U_B^{1-x} U_C^{x}} \right].
\]

In the alternative, constant-entropy transition from state A to state D, the system delivers work \( U_A - U_D \) to an external, purely mechanical device (such as a weight on a frictionless pulley). At the same time, some energy in the form of heat must be transferred reversibly from subsystem 2 to subsystem 1, since these have constant volumes but reach the same temperature \( T_D \).
It sounds like one or more cannot engine must be coming into play, so let's remind ourselves how these function. As the working fluid of a Carnot engine we can use \( n \gg 1 \) mole some ideal gas. By expanding isothermally while in contact with a higher-temperature heat source, the gas acquires (negative) work

\[
W_a = - \int_{v_1}^{v_2} P \, dV = - \int_{v_1}^{v_2} \frac{mR T_h}{V} \, dV
\]

\[
= -mRT_h \ln \left( \frac{V_2}{V_1} \right)
\]

Because the working fluid is an ideal gas \((U = CVT)\), its internal energy does not change during this isothermal expansion, so it absorbs heat \(Q_a = mRT_h \ln \left( \frac{V_2}{V_1} \right)\) from the higher-temperature source.

In the next step, 4, the gas expands adiabatically:

\[
\frac{dU}{T} = -P \, dV \quad \text{here, so} \quad CV \, dT = -\frac{m \, RT}{V} \, dV \quad \text{whence}
\]

\[
CV \ln \frac{T_2}{T_h} = -mR \ln \frac{V_3}{V_2} \quad \Rightarrow \quad \left( \frac{T_2}{T_h} \right)^{CV/mR} = \frac{V_2}{V_3} \quad \text{or} \quad T = \frac{CV/mR}{V} \text{ constant}
\]
The (negative) work acquired by the gas in this step equals its (negative) energy change:

$$W_b = \Delta U_b = - \int_{V_2}^{V_3} P \, dV = - \int_{V_2}^{V_3} \frac{mRT}{V} \, dV.$$  

Let \( V = \text{const.} \cdot T - \frac{c_v}{mR} \)

$$\Rightarrow \int V = - \frac{c_v}{mR} \cdot \text{const.} \cdot T - \frac{c_v}{mR} \cdot T = \frac{T_e}{T_h} \cdot \int_{T_h}^{T_e} dT = c_v (T_e - T_h),$$

as we could have found more simply from

$$\Delta U_b = \int_{T_h}^{T_e} c_v \, dT.$$  (why doesn't it matter that the volume changes in this process?)

\( Q_b = 0 \), of course, since the transition from \( \text{(2)} \to \text{(3)} \) occurs adiabatically.

In the isothermal compression at \( T_e \) of step c, we have

$$W_c = mRT_e \ln \frac{V_4}{V_3} = -Q_c;$$

but what is \( V_4 \) ? Notice that, because \( \text{(1)} \) and \( \text{(4)} \) are connected by an adiabatic process,

$$\frac{V_1}{V_4} = \left( \frac{T_e}{T_h} \right)^{\frac{c_v}{mR}} \Rightarrow \frac{V_4}{V_3} = \frac{V_1}{V_2}.$$
Thus \[ W_a = -\frac{T_a}{T_n} \cdot W_a = \frac{T_e}{T_n} \cdot Q_a = -Q_c. \]

In step a, an adiabatic compression, \( Q_d = 0 \) and \( W_d = c_v(T_h - T_e) \).

In this reversible, cyclic process the work of steps b and c cancel so the Carnot engine performs work

\[ -W_a - W_c = mR(T_h - T_e) \ln \left( \frac{V_2}{V_1} \right) \]

\[ = (1 - \frac{T_e}{T_h})Q_a. \]

(If the \( T_e \) heat-sink were at absolute zero, all of the heat absorbed at \( T_h \) would be converted into work, and the engine would be 100% efficient!)

It's more helpful in the present context to view this cycle of alternating isothermal and adiabatic transformations as a plot in the TS-plane:

[Diagram of TS-plane cycle 1-2-3-4-a-b-c-d-s]
The work done by the gas in this cycle is equal to the area enclosed in the TS-plane or the PV-plane. Can you prove these statements?

Now we're well positioned to provide a concrete example of how heat might be reversibly transferred from the cooling, higher-temperature subsystem (2) to the warming, lower-temperature one (4) in order to effect the A → D transition mentioned on p. 32.

We can determine the equilibrium temperature $T_D$ as follows: Since the heat capacity of our mole of monatomic ideal gas is $3R/2$ (see p. 29), the entropy of state C is

$$ S_C = S_B + \int \frac{dU}{T} = S_B + \frac{3}{2} R \int \frac{dT}{T} = S_B + \frac{3}{2} R \ln \frac{T_C}{T_B}, $$

and, similarly, the entropy of state D is

$$ S_D = S_B + \frac{3}{2} R \ln \frac{T_D}{T_B}. $$
But \( S_D = S_A = (1-x)S_B + xS_d \)

\[
= (1-x)S_B + xS_B + x \frac{3R}{2} \ln \frac{T_c}{T_B} \\
= S_B + \frac{3}{2} R \ln \left( \frac{T_c}{T_B} \right)^x.
\]

Equating these two expressions for \( S_D \) tells us that \( \frac{T_D}{T_B} = \left( \frac{T_c}{T_B} \right)^x \) or \( T_D = T_B \left( \frac{T_c}{T_B} \right)^x \).

This is the temperature to which subsystem 1 is reversibly heated and subsystem 2 reversibly cooled, while (somehow, but how?) performing work \( U_A - U_D \).

As an illustrative case, let's imagine that \( T_c = 4T_B \) and \( x = \frac{1}{2} \). Then

\[ T_D = T_B \left( 4^{1/2} \right) = 2T_B \]

During the heating process, the entropy of subsystem 1 grows as

\[
S_D = (1-x) \left[ S_B + \frac{3}{2} R \ln \frac{T_c}{T_B} \right] \\
= \frac{1}{2} \left[ S_B + \frac{3}{2} R \ln \frac{T_c}{T_B} \right].
\]
Using the fact that, in the present instance,

\[ S_D = S_B + \frac{3}{2} R \ln 2 \implies S_B = S_D - \frac{3}{2} R \ln 2, \]

we have

\[ S_1 = \frac{1}{2} \left[ S_D - \frac{3}{2} R \ln 2 + \frac{3}{2} R \ln \frac{T_1}{T_D/2} \right] \]

\[ = \frac{1}{2} \left[ S_D + \frac{3}{2} R \ln \frac{T_1}{T_D} \right] \]

\[ \implies T_1 = T_D e^{\frac{4}{3R} (S_1 - S_D/2)} \]

which one could have obtained by replacing B with D at the bottom of page 37.

A similar analysis shows that, during the cooling process,

\[ T_2 = T_D e^{\frac{4}{3R} (S_2 - S_D/2)} \]

In each case the temperature of the subsystem grows exponentially with its entropy:

![Graph showing exponential growth of temperature with entropy](image)
Comparison of these T-S curves with the cannot-cyle plot on p. 35 immediately suggests that
one could effect the reversible transfer of
heat $\frac{3}{2}R(T_0 - T_0) \cdot \frac{1}{2} = \frac{1}{2} (U_p - U_b)$ to subsystem 1.
The reversible expulsion of heat $\frac{1}{2} (U_c - U_0)$ from
subsystem 2, and the delivery of work $U_A - U_b$
$= \frac{1}{2} U_B + \frac{1}{2} U_c - U_0$ to an external work reservoir
through the action of a sequence of a large number $N$
of Carnot engines, with each one operating between
the temperatures $T_h$ (just below the current $T_2$)
and $T_L$ (just above the current $T_1$) and transferring
a small amount of entropy
$\Delta S = \frac{(S_c/2 - S_0/2)}{N} = \frac{(S_0/2 - S_b/2)}{N}$
from the higher temperature subsystem to the lower.
The work done by each engine is equal to the
area of the corresponding tall, skinny rectangle
in the plot above. In the limit of very large $N$, the total work delivered becomes the area
between the subsystems' T-S curves.
Intensive Variables

The differential of the fundamental relation,

\[ U = U(x_1, x_2, \ldots, x_{r+1}) \]

in the energy scheme is

\[ dU = \sum_{i=1}^{r+1} \frac{\partial U}{\partial x_i} dx_i \]

\[ dU = \sum_{i=1}^{r+1} P_i dx_i \]

where \( P_i \) is the intensity conjugate to the extensive variable \( x_i \).

With \( x_1 = S \), \( x_2 = V \), and \( x_{j+2} = N_j \) for \( j = 1, \ldots, c \),

the energy differential can be written

\[ dU = T \, ds - p \, dV + m_1 \, dN_1 + \cdots + m_c \, dN_c \]

Recall that \( T = \frac{\partial U}{\partial s} \) and \( p = -\frac{\partial U}{\partial V} \)

The intensity conjugate to the entropy is the temperature.

The intensity conjugate to the volume is negative the pressure.

The intensity \( m_j \) is the mole-number \( N_j \) is the chemical potential \( \mu_j \).

Working from the postulates already enunciated, it is possible to derive a number of relations obeyed by the intensities and illustrate some aspects of their physical behavior.
In a composite system whose subsystems are separated by partitions that are non-restrictive with respect to \( X_2 \), the variations \( \delta X_2^{(a)} \) obey the relation

\[
\sum_a \delta X_2^{(a)} = 0 \quad \text{(*)}
\]
during any virtual process, whereas \( \delta X_i^{(a)} = 0 \) for \( i \neq 2 \) and all \( a \). The equilibrium condition in the energy scheme is

\[
\delta W = \sum_a \delta U^{(a)} = 0,
\]
subject to the constraint (\( \text{(*)} \)). Equivalently, for some undetermined multiplier \( \lambda_2 \), this equilibrium can be identified with an extremum of

\[
0 - \lambda_2 \sum_a X_2^{(a)}
\]
over unconstrained variations of \( X_2^{(a)} \):

\[
0 = \delta U - \lambda_2 \sum_a \delta X_2^{(a)} = \sum_a (P_2^{(a)} - \lambda_2) \delta X_2^{(a)}.
\]

Thus, when all the subsystems are free to exchange the quantity \( X_2 \), we arrive at the equilibrium condition

\[
P_2^{(a)} = \lambda_2 = \text{constant for all } a.
\]

The size extensive variables of the various subsystems assume values that insure that their conjugate instensities are all equal.